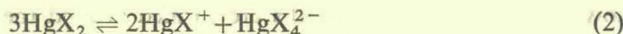


EFFECT OF PRESSURE ON THE DEGREE OF IONIZATION

Comparison of vapour-phase and liquid-phase Raman spectra shows that, at atmospheric pressure, the fused mercuric halides consist predominantly of linear molecules HgX_2 .^{6, 10-13} The conductivity has been attributed^{1, 6} to slight self-ionization with formation of complex ions



and, to a lesser extent,



The ions HgX^+ , HgX_3^- and HgX_4^{2-} cannot be detected in the pure melts by Raman spectroscopy, but HgX^+ has been found in aqueous solutions of HgX_2 with added $\text{Hg}(\text{ClO}_4)_2$,¹⁴ and spectra due to HgX_3^- , and ultimately HgX_4^{2-} , appear when alkali metal halides are added to molten HgX_2 .^{15, 16} Band intensity data¹⁵ indicate that equilibrium (2) may be ignored in pure HgX_2 melts at atmospheric pressure.

Previous work on fully ionized melts, such as the alkali metal nitrates² or halides,¹⁷ has shown that a pressure of 1000 bar reduces the conductivity by up to 10 %. This decrease is attributed to a reduction in the mobilities of the ions, caused by the increase in density. The conductivities of non-aqueous solutions of fully dissociated electrolytes usually decrease with pressure for the same reason.¹⁸⁻²¹ For aqueous solutions of strong electrolytes, increases in conductivity with pressure which are sometimes observed are attributed to changes in solvent structure or to the operation of a Grotthuss mechanism, e.g. for proton transfer.⁵ For weak electrolyte solutions, the degree of dissociation increases with pressure, because the solvation of the ions involves a net reduction in the volume of the system.^{22, 23} The same consideration applies to the self-ionization of molecular liquids such as water.²⁴ We now consider whether our results can be accounted for in terms of the displacement of equilibrium (1) to the right with pressure. For this purpose we ignore for the present the effect of pressure on ion mobilities.

Let c denote the concentration, a the activity and f_{\pm} the mean ion activity coefficient of the ions HgX^+ and HgX_3^- . For equilibrium (1),

$$K = a_{\text{HgX}^+} a_{\text{HgX}_3^-} / a_{\text{HgX}_2}^2$$

Since the ionic concentrations are relatively small, we ignore changes in the activity of the molecular species and write

$$K' = a_{\text{HgX}^+} a_{\text{HgX}_3^-} = c^2 f_{\pm}^2$$

Using standard thermodynamics, the change in standard partial molar volume when ionization (1) takes place is given by

$$\overline{\Delta V}^\circ = -RT(\partial \ln K' / \partial P)_T = -2RT(\partial \ln c / \partial P)_T - 2RT(\partial \ln f_{\pm} / \partial P)_T \quad (3)$$

Assuming, as a first approximation, that the ion mobilities are independent of pressure at constant temperature,

$$-2RT(\partial \ln c / \partial P)_T \approx -2RT(\partial \ln \kappa / \partial P)_T = 2\Delta V_\kappa \quad (4)$$

Comparing eqn (3) and eqn (4), one obtains

$$2\Delta V_\kappa = \overline{\Delta V}^\circ + 2RT(\partial \ln f_{\pm} / \partial P)_T. \quad (5)$$

We now estimate the volume terms on the right side of eqn (5), and compare them with $2\Delta V_\kappa$ determined experimentally. $\overline{\Delta V}^\circ$ may be considered in two parts

$$\overline{\Delta V}^\circ = \overline{\Delta V}_1^\circ + \overline{\Delta V}_2^\circ.$$

$\overline{\Delta V}_1^\circ$ is the volume of the ions HgX^+ and HgX_3^- minus the volume of two HgX_2 molecules, and has been calculated from the appropriate bond lengths and van der Waals radii. The ions HgX_3^- were taken to be planar and trigonal. The van der Waals radii used were ²⁵ (in 10^{-10} m): Hg, 1.25; Cl, 1.80; Br, 1.95; I, 2.15. As table 1 shows, $\overline{\Delta V}_1^\circ$ is less than 1 ml mol^{-1} for all three equilibria, so this contribution to $\overline{\Delta V}^\circ$ is negligible. For the remainder of this section, $\overline{\Delta V}^\circ$ is equated with $\overline{\Delta V}_2^\circ$. $\overline{\Delta V}_2^\circ$ is the volume change in the solvent when ionization occurs, the "solvent" in this case being molecular HgX_2 . $\overline{\Delta V}_2^\circ$ is negative, and represents the electrostriction of the solvent when solvation sheaths are formed around the ions. The standard partial molar free energy of solvation of a spherical ion of charge ze and radius r , in a solvent of permittivity ϵ is given by the Born equation

$$\overline{\Delta G}^\circ = -\frac{Ne^2z^2}{2r}\left(1 - \frac{1}{\epsilon}\right)$$

Differentiating with respect to pressure, we obtain for the standard partial molar volume change on solvation ²⁶

$$\overline{\Delta V}_2^\circ = \left(\frac{\partial \overline{\Delta G}^\circ}{\partial p}\right)_T = \sum_{\text{ions}} \left[\frac{Ne^2z^2}{2r^2} \left(1 - \frac{1}{\epsilon}\right) \left(\frac{\partial r}{\partial p}\right)_T - \frac{Ne^2z^2}{2r\epsilon^2} \left(\frac{\partial \epsilon}{\partial p}\right)_T \right] \quad (6)$$

The terms in the square bracket can be evaluated if ϵ , r and their pressure derivatives are known. For the mercuric halides, experimental values of ϵ are available only for the solids.²⁷ Since the crystals contain non-polar molecules HgX_2 (in the case of HgI_2 , this applies to the yellow modification), ϵ for the liquids can be estimated by assuming that the Clausius-Mosotti function, $V_m(\epsilon - 1)/(\epsilon + 2)$, undergoes no change when the substance is melted. The density data used were taken from Janz and McIntyre.⁶ Likewise, $(\partial \epsilon / \partial p)_T$ can be found by assuming that the Clausius-Mosotti function is invariant with pressure. The resulting expression for $(\partial \epsilon / \partial p)_T$ is

$$(\partial \epsilon / \partial p)_T = [(\epsilon - 1)(\epsilon + 2)\beta_T]/3 \quad (7)$$

where β_T is the isothermal compressibility. To check the validity of this approximation, $(\partial \epsilon / \partial p)_T$ was calculated for carbon disulphide and for benzene, using eqn (7) and published values of ϵ and β_T , and was then compared with $(\partial \epsilon / \partial p)_T$ obtained by direct measurement. The calculated value differed from the measured one by 3 % for CS_2 ²⁸ and by 10 % for benzene.²⁹ This accuracy is sufficient for the present purpose, having regard to the other approximations inherent in the Born model for solvation.

The isothermal compressibilities of the molten mercuric halides were recalculated from ultrasonic velocity data reported by Bockris *et al.*,³⁰ using the equations and constant pressure specific heats given in their paper, but taking densities and expansivities from ref. 6. The value of β_T for HgI_2 listed by Bockris appears to have been wrongly calculated from the experimental data. The term $(\partial r / \partial p)_T$ in eqn (6) could be estimated from compressibility measurements on the solid mercuric halides, but unfortunately none have been made. The values adopted were based on the compressibilities of solid TlCl , TlBr and TlI .³¹ As table 1 shows, the contribution to $\overline{\Delta V}^\circ$ from this term is relatively small, so the final value obtained for $\overline{\Delta V}^\circ$ is not strongly influenced by errors in $(\partial r / \partial p)_T$.

The Born equation refers to spherical ions of radius r . Neither HgX^+ nor HgX_3^- is spherical. Two methods of calculation were used:

Method 1. For each ion, the value of r used was that of a sphere having the same volume,